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Molybdenum Disubstituted Alkylidene Complexes

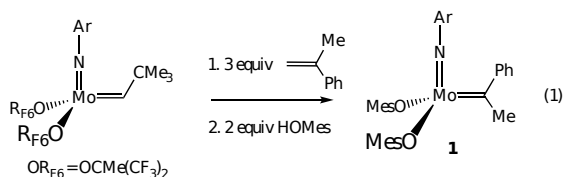
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ABSTRACT: Through relatively straightforward techniques that begin with $\text{Mo}(\text{NAr})(\text{CH-}t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) we have prepared $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OMesityl})_2$, $[\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2]_2$, $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$, $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{bipyridyl})$, $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})_2(\text{bipyridyl})$, $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ ($\text{OHMT} = \text{O-}2,6\text{-(}2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$), and $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Pyrrolide})(\text{OHMT})$. X-ray studies reveal that in five compounds the alkylidene isomer (**A**) is that in which the phenyl group in the alkylidene points toward the imido nitrogen. In $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ the isomer in which the methyl group points toward the imido nitrogen (isomer **B**) has cocrystallized with isomer **A** (12%). In two 14e compounds that contain isomer **A** the $\text{Mo}=\text{C-C}$ angles differ by $30\text{--}36^\circ$, consistent with a $\text{Mo}\cdots\text{C-H}_\beta$ agostic interaction. Several of the complexes reported here react readily with ethylene, 1-decene, or cyclooctene to give the expected products, thus confirming their viability as initiators or intermediates in metathesis reactions.

The extensive chemistry of alkylidene complexes that is relevant to olefin metathesis is virtually entirely concerned with complexes that contain one ($\text{M}=\text{CHR}$) or two ($\text{M}=\text{CH}_2$) α protons.¹ However, one of the remaining challenges in olefin metathesis is the synthesis of tetrasubstituted olefins,² a reaction that would require formation of an intermediate $\alpha,\alpha,\beta,\beta$ tetrasubstituted metallacyclobutane complex from a disubstituted alkylidene intermediate. Molybdenum d^0 disubstituted alkylidene complexes are limited to those formed through addition of $\text{H}_2\text{C}=\text{CRPh}$ ($\text{R} = \text{Me}$ or Ph) to neopentylidene or neophylidene complexes ($\text{Mo}(\text{NAr})[\text{CMePh}][\text{OCMe}(\text{CF}_3)_2]_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$)³ and $\text{Mo}(\text{NAdamantyl})(\text{CPhR})[\text{OCH}(\text{CF}_3)_2]_2(2,4\text{-Lutidine})$ ⁴ or through a reaction between an alkylidene and one equivalent of an alkyne.⁴ No disubstituted alkylidene complex has been structurally characterized or explored in olefin metathesis reactions. For these reasons we decided to address from today's perspective the stability, reactivity, and viability in metathesis reactions of d^0 molybdenum imido disubstituted alkylidene complexes.

Addition of α -methyl styrene to $\text{Mo}(\text{NAr})(\text{CH-}t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$ to give $\text{Mo}(\text{NAr})(\text{CMePh})[\text{OCMe}(\text{CF}_3)_2]_2$ ³ followed by addition of 2,4,6-trimethylphenol (MesitylOH) gave $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OMes})_2$ (**1**), which was isolated in 74% yield as red plates (eq 1). Proton and carbon NMR spectra



showed **1** to be one isomer with an alkylidene α carbon resonance at 263.1 ppm (Table 1). An X-ray structural determination (Figure 1) showed that in **1** the alkylidene phenyl group points toward the imido ligand (isomer **A**) with $\text{Mo}=\text{C}_\alpha = 1.905(1) \text{ \AA}$ (Table 1). The $\text{M}=\text{C-C}$ angles are significantly different from one another with $\text{M}=\text{C-C}_{\text{Me}} = 102.38(8)^\circ$ and $\text{M}=\text{C-C}_{\text{ipso}} = 138.71(8)^\circ$ ($\Delta = 36.3^\circ$). The $\text{M}=\text{C-C}_{\text{Me}}$ angle, $\text{Mo}\cdots\text{C}_\beta$ distance (2.68 Å), $\text{Mo}\cdots\text{H}_\beta$ distance (2.51 Å), and $\text{Mo}\cdots\text{H}_\beta\text{-C}_\beta$ angle (89.2°) (H_β was located) are all consistent with an agostic interaction⁵ between an alkylidene methyl proton in the N-Mo-C plane and the metal. The $\text{Mo}\cdots\text{C-H}_\beta$ interaction is related to a $\text{Mo}=\text{C-H}_\alpha$ agostic interaction in a terminal alkylidene in the *syn* form in which the substituent points toward the imido ligand.^{1a} Rearrangement of a $\text{Mo}=\text{CHR}$ complex to an olefin when R contains a β hydrogen atom has not been observed, possibly because of a competing $\text{Mo}=\text{C-H}_\alpha$ agostic interaction. The fact that the alkylidene in **1** does not rearrange to styrene suggests that such a rearrangement is inherently disfavored, not simply blocked by a C-H_α agostic interaction.

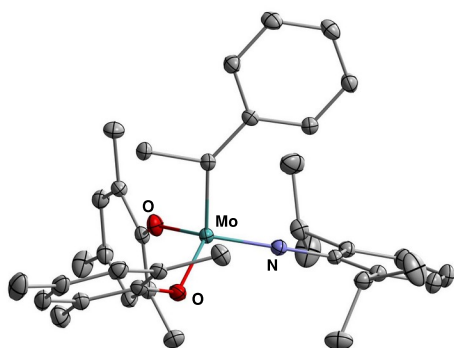


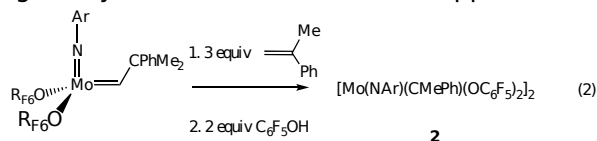
Figure 1. Thermal ellipsoid plot (50%) of **1**. Unlabeled ellipsoids correspond to carbon. Solvent molecules and hydrogen atoms have been omitted for clarity.

Table 1

Compd	Δ	M=C (Å) δC_{α}	M-C-C _{Me}	M-C-C _{ipso}
1	1.905(1) 36.3	263.1 ^a	102.38(8)°	138.71(8)°
2(MeCN)_B ^b	1.942(4) 12.3	316.8 ^c	127.40(3)	115.1(3)
2(bipy)	1.969(2) 2.6316.9 ^d		122.4(1)°	125.0(1)°
3(bipy)	2.011(6) 0.4324.2 ^d		123.5(5)°	123.1(5)°
4(MeCN)	1.929(2) 18.4	323.7 ^c	112.8(1)°	131.2(1)°
5	1.903(3) 29.7	290.6 ^a	105.7(2)	135.4(2)°

^aC₆D₆ ^bIsomer **B** ^cCD₃CN; See SI for discussion
^dCD₂Cl₂.

The reaction sequence shown in equation 2 led to formation of a yellow solid whose insolubility in pentane, diethyl ether, benzene, and dichloromethane, along with its reaction with acetonitrile to yield Mo(NAr)(CMePh)(OC₆F₅)₂(MeCN) (**2(MeCN)**) suggests that it is [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ (eq 2). [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ dissolves readily in THF-*d*₈ to give a solution that we propose contains an adduct, Mo(NAr)(CMePh)(OC₆F₅)₂(THF)_x (x = 1 or 2), a ¹³C NMR spectrum of which at -40° C shows a single alkylidene resonance at 310.7 ppm.



A structural study of **2(MeCN)** (Figure 2) showed it to be a cocrystallized mixture of the isomer with the *methyl* group in the alkylidene pointing toward the imido nitrogen (isomer **B**, 88%; M=C-C_{Me} = 127.40(3)°, M=C-C_{ipso} = 115.10(3)°, Δ = 12.3°) and alkylidene isomer **A**. (Analogous data could not be extracted reliably for isomer **A** in this disordered structure.). The NMR data for **2(MeCN)** in acetonitrile-*d*₃ suggest that two isomers of **2(MeCN)₂** can form and that acetonitrile slowly

destroys the alkylidene, a type of reaction that has been documented for analogous W alkylidenes.^{6b} The rates of exchange of donor ligands in **16e** and **18e** adducts and the rates of interconversion of isomers **A** and **B** in various circumstances remain to be elucidated.

A structural study of the readily formed **18e** bipy adduct, Mo(NAr)(CMePh)(OC₆F₅)₂(bipy) (**2(bipy)**, eq 3, Figure 3), showed it to contain alkylidene isomer **A** with (not surprisingly) no evidence for any CH_β interaction and alkylidene M-C-C angles that are approximately equivalent (Δ = 2.6°, Table 1). Bipy adducts of neopentylidene or neophylidene imido complexes are known,⁶ but their formation can be complicated by deprotonation of an alkylidene to give an alkylidyne complex.^{6a}

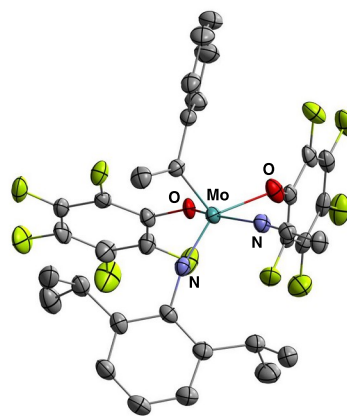
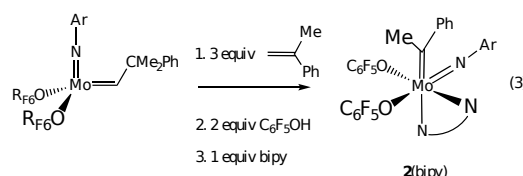


Figure 2. Thermal ellipsoid plot (50%) of **2(MeCN)_B** (isomer **B**). Unlabeled gray ellipsoids correspond to carbon, green to fluorine. Solvent molecules and hydrogen atoms have been omitted for clarity.

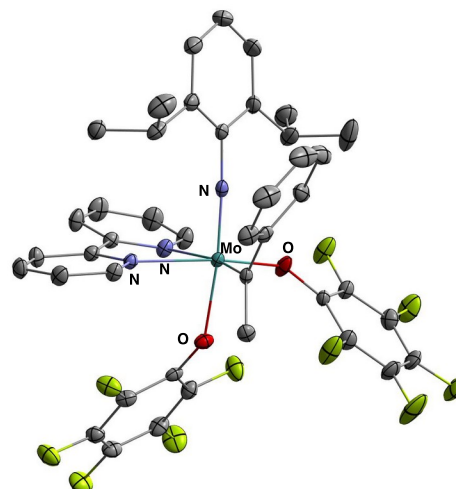
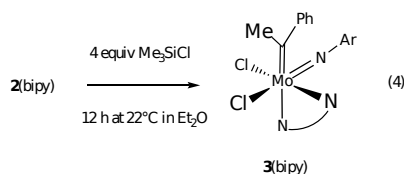


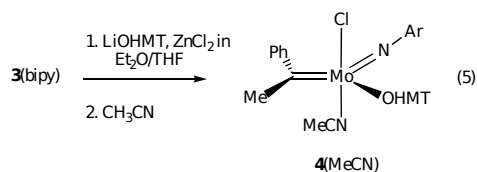
Figure 3. Thermal ellipsoid plot (50%) of **2(bipy)**. Unlabeled gray ellipsoids correspond to carbon, green to fluorine.

fluorine. Solvent molecules and hydrogen atoms have been omitted for clarity.

Addition of TMSCl to **2**(bipy) in diethyl ether yielded **3**(bipy) (eq 4), the dichloride analog of **2**(bipy). Similar conversions have been achieved with other 18e neophylidene NAr bispentafluorophenoxide complexes.^{6b} An X-ray study (see SI for a Figure and details) showed the structure of **3**(bipy) to be analogous to that of **2**(bipy), *i.e.*, it contains alkylidene isomer **A** with approximately equal Mo-C-C angles ($\Delta = 0.4^\circ$, Table 1).



The reaction shown in equation 5 produced the monochloride hexamethylterphenoxide (OHMT = O-2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃) complex as an acetonitrile adduct, **4**(MeCN). A structural study of **4**(MeCN) (Figure 4) showed it to contain alkylidene isomer **A** (Mo=C = 1.929(2), $\tau^7 = 0.22$). This structure is overall similar to the structure of Mo(NAr)(CHCMe₂Ph)(OHMT)(Cl)(*t*-BuCN) (Mo=C = 1.890(1) Å, $\tau = 0.21$).^{6b} As a consequence of the 16e count in **4**(MeCN) the M-C-C_{Me} and M-C-C_{ipso} differ from one another to a significant degree ($\Delta = 18.4^\circ$, Table 1), but not nearly as much as in 14e **1**.



Compound **4**(MeCN) reacts with lithium pyrrolide to form 14e Mo(NAr)(CMePh)(OHMT)(pyr) (**5**; equation 6), a structural study of which shows it to contain alkylidene isomer **A** (Fig 5) with M=C-C_{Me} and M=C-C_{ipso} angles similar to those found in 14e **1**, but with a smaller difference ($\Delta = 29.7^\circ$, Table 1), perhaps as a consequence of pyrrolide being a better σ electron donor than an aryloxide.

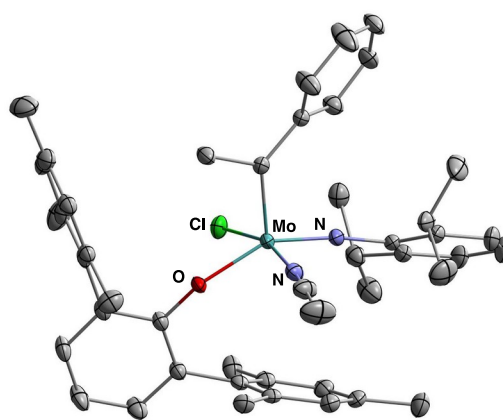
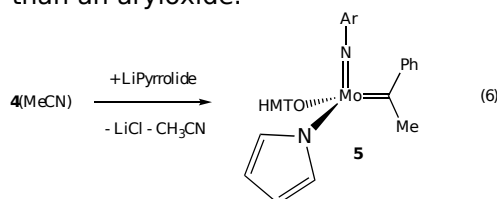


Figure 4. Thermal ellipsoid plot (50%) of **4**(MeCN). Unlabeled ellipsoids correspond to carbon. Solvent molecules and hydrogen atoms have been omitted for clarity.

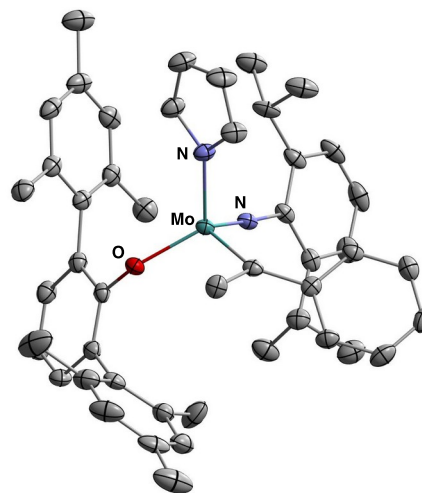


Figure 5. Thermal ellipsoid plot (50%) of **5**. Unlabeled ellipsoids correspond to carbon. Solvent molecules and hydrogen atoms have been omitted for clarity.

We have explored in a preliminary manner the reactions of several Mo=CMePh complexes reported here with olefins. (See SI for details.) [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ in THF-*d*₈ reacts rapidly with ethylene (<10 min under 1 atm) to give one equivalent of α -methyl styrene and a green solution whose NMR spectra suggest that the final Mo-containing product is either an ethylene complex or a molybdacyclopentane complex, examples of which are known.⁸ Resonances for inequivalent methylene protons in an unstable Mo(CH₂) complex are observed in the spectrum recorded after 10 minutes. Mo(NAr)(CMePh)(Cl)(OHMT) (**4**(MeCN)) also reacts with ethylene to yield α -methylstyrene after 10 min; all **4**(MeCN) is consumed after two hours. ROMP of cyclooctene (~20 equiv) by Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) or Mo(NAr)(CMePh)(OC₆F₅)₂(THF)_x as the initiator in C₆D₆ was essentially complete when examined by proton NMR after 20 minutes.

1-Decene (100 equiv) also was homocoupled by each in uncapped vials (under N₂) to give a mixture of *E* and *Z* 9-octadecene in >90% yields. The reaction initiated by Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) is much faster, being 86% complete in 20 min. The amount of reduction by the ethylene generated in the homocoupling reactions, as described above, was not determined.

We conclude that Mo imido disubstituted alkylidenes can be prepared readily through reactions analogous to those reported for the many monosubstituted alkylidene complexes that have been prepared and studied^{1a,b,c} and that they react readily with olefins to give metathesis products. The examples reported here include monochloride aryloxide and monopyrrolide aryloxide complexes, which have been found relatively recently to promote cross-metathesis reactions that involve electron-poor olefins.⁹ The absence of an α proton in a disubstituted alkylidene prevents complications that arise in some M=CHR chemistry, one being deprotonation complex with either an internal nucleophile/ligand or external nucleophile to yield an alkylidyne.^{6a} Decomposition through alkylidene coupling to give a tetrasubstituted olefin is also likely to be slower for disubstituted alkylidene complexes than for monosubstituted alkylidene complexes.¹⁰ However, the ultimate goal, catalytic formation of tetrasubstituted olefins, will require disubstituted alkylidenes to be able to form an $\alpha,\alpha,\beta,\beta$ tetrasubstituted metallacyclobutane intermediate. We look forward to further synthetic, mechanistic, reactivity, and catalytic studies of these and other disubstituted alkylidenes with that goal in mind.

ASSOCIATED CONTENT

Supporting Information Synthesis details and NMR data for all compounds, and details of X-ray studies.

Accession Codes

CCDC 1965163, 1965162, 1965159, 1965158, 1965160 and 1965161 contain the supplementary crystallographic data for **1**, **2**(MeCN), **2**(bipy), **3**(bipy), **4**(MeCN) and **5**, respectively. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

JWT performed all synthetic work while CT performed all X-ray structural studies.

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Notes

The authors declare no competing financial interest.

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